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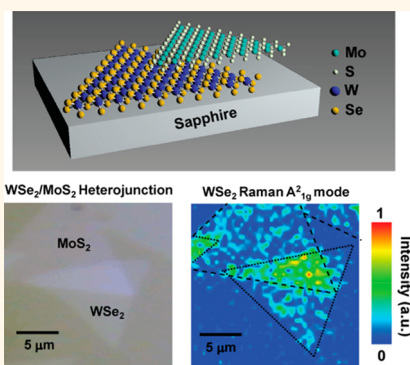
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Spectroscopic Signatures for Interlayer Coupling in MoS₂–WSe₂ van der Waals Stacking

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ABSTRACT Stacking of MoS₂ and WSe₂ monolayers is conducted by transferring triangular MoS₂ monolayers on top of WSe₂ monolayers, all grown by chemical vapor deposition (CVD). Raman spectroscopy and photoluminescence (PL) studies reveal that these mechanically stacked monolayers are not closely coupled, but after a thermal treatment at 300 °C, it is possible to produce van der Waals solids consisting of two interacting transition metal dichalcogenide (TMD) monolayers. The layer-number sensitive Raman out-of-plane mode A²_{1g} for WSe₂ (309 cm⁻¹) is found sensitive to the coupling between two TMD monolayers. The presence of interlayer excitonic emissions and the changes in other intrinsic Raman modes such as E'' for MoS₂ at 286 cm⁻¹ and A²_{1g} for MoS₂ at around 463 cm⁻¹ confirm the enhancement of the interlayer coupling.



KEYWORDS: transition metal dichalcogenides · tungsten diselenides · molybdenum disulfide · van der Waals stacking · heterojunction · interlayer coupling

Semiconducting transition metal dichalcogenide (STMD) layered materials exhibit unique layer-dependent electronic and optical properties.^{1–12} For example, molybdenum disulfide (MoS₂) exhibits an indirect bandgap of 1.2 eV in bulk, but it becomes a direct gap semiconductor (bandgap = 1.8 eV) when thinned to a monolayer.^{4,8} Hence, monolayer MoS₂ transistors have been fabricated and these devices have showed excellent current on/off ratios.^{10–12} MoS₂ is known as an *n*-type semiconductor due to the presence of S vacancies. Another STMD, tungsten diselenide (WSe₂), has just started to attract the attention of numerous scientists due to its *p*-type characteristics.^{2,13} In addition to the mechanical exfoliation method to prepare STMD layers, recent developments in the scalable synthesis of STMD monolayers using chemical vapor deposition (CVD) opened up the possibility to form large area of STMD monolayers that could result in fabrication of flexible

electronic devices and photodetectors.^{1,2,14} Furthermore, it is also possible to envisage building unprecedented solids by stacking monolayers of different 2-D systems one on top of another (*e.g.*, TMDs, h-BN and graphene).^{15–21} Such stacked heterostructures based on atomically thin 2D layers are fundamentally different since only van der Waals interactions exist at the interfaces. Therefore, these layered materials (termed also van der Waals solids) enable the preparation of high-quality heterointerfaces without the need of fulfilling an atomic commensurability,^{17,18,22} thus making the structure construction easily achievable. Very recently, MoSe₂/WSe₂ optical studies were performed,²³ and other optoelectronic devices based on WSe₂/MoS₂ *p–n* junction were also proposed.^{24–27} Interestingly, the gate-tunable diode-like current rectification and a photovoltaic response have been recently observed in WSe₂/MoS₂ heterojunctions.^{24–26} It should be noted that the optical

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and electrical properties of TMD heterojunctions strongly depend on the interaction among layers, and efforts aiming at elucidating their proper characterization is currently underway.

In this paper, we demonstrate that it is possible to build van der Waals solids by first stacking CVD-grown MoS_2 on WSe_2 monolayers, followed by thermal annealing. The layer-number sensitive Raman mode A_{1g}^2 for WSe_2 at around 309 cm^{-1} (out-of-plane mode) appears to be excellent parameters when evaluating a good coupling between monolayers. The Raman modes for bulk MoS_2 at *ca.* 463 cm^{-1} (A_{1g}^2) and at *ca.* 283 cm^{-1} (E'') are also enhanced by interlayer coupling. In addition, the interlayer excitonic peak observed in photoluminescence (PL) confirms the coupling between two TMD monolayers and a band diagram of the $\text{MoS}_2/\text{WSe}_2$ heterojunction and the exciton binding energies for each composition are proposed.

RESULTS AND DISCUSSION

Preparation and Characterizations of Heterojunction. Triangular WSe_2 and MoS_2 single crystalline monolayers with the lateral dimension of few tens of micrometers were synthesized on c-plane sapphire substrates by CVD.^{1,2} In brief, transition metal trioxides (MoO_3 or WO_3) were vaporized and reacted with the S or Se vapor in a hot-wall furnace under a controlled gaseous environment to form MoS_2 or WSe_2 monolayers (see details in Methods). To build a van der Waals solid (or vertical heterojunction of MoS_2 on WSe_2), as schematically illustrated in Figure 1a, we first detached as-synthesized MoS_2 triangular islands using PMMA. In particular, a layer of PMMA was spin-coated on MoS_2 followed by dipping it in NaOH so as to release the PMMA-supported MoS_2 from the substrates. The PMMA supported- MoS_2 was then mechanically transferred onto WSe_2 flakes followed by the removal/cleaning of PMMA.³ Figure 1b is the optical micrograph (OM) showing the mechanically stacked $\text{MoS}_2/\text{WSe}_2$ monolayers, in which it is possible to distinguish the stacked layers by noticing a color contrast. Supporting Information Figure S1 shows the atomic force microscopy (AFM) image of as-transferred $\text{MoS}_2/\text{WSe}_2$, where the surface of the sample is covered with residuals and adsorbates. In this context, it has been demonstrated by scanning tunneling microscopy (STM) that the majority of the adsorbates and residuals can be removed after thermal annealing at elevated temperatures.²⁸ Therefore, as-prepared $\text{MoS}_2/\text{WSe}_2$ samples were then annealed in an hydrogen/Ar environment (atmosphere pressure; $\text{H}_2/\text{Ar} = 1:4$) at $300\text{ }^\circ\text{C}$ for 4 h. The detailed fabrication process is described in Methods.

The AFM image and cross-sectional profile of the $\text{MoS}_2/\text{WSe}_2$ heterojunction are shown in Figure 1c, demonstrating that both WSe_2 and MoS_2 are indeed monolayers (thickness for each is around $0.6\text{--}0.7\text{ nm}$). The AFM image also shows that the individual flakes

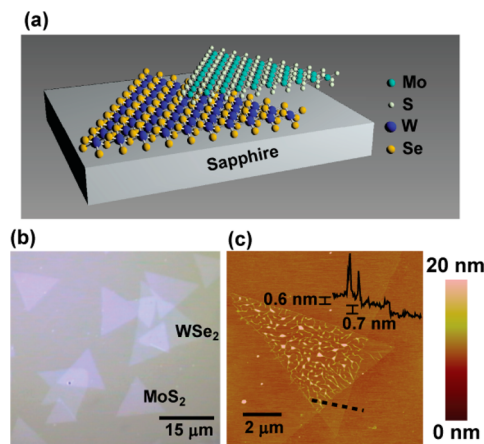


Figure 1. Representation of the vertical heterojunction consisting of MoS_2 monolayers deposited on top of WSe_2 monolayers: (a) schematic illustration of the $\text{MoS}_2/\text{WSe}_2$ van der Waals heterojunction; (b) optical micrograph of the mechanically stacked $\text{MoS}_2/\text{WSe}_2$ structure after thermal annealing, and (c) AFM image of the $\text{MoS}_2/\text{WSe}_2$ heterojunction. The cross-sectional height profile along the dashed line indicates that each layer is about $0.6\text{--}0.7\text{ nm}$ in thickness.

are clean and without cracks or holes after the H_2/Ar thermal treatment. Interestingly, the corrugated structures are found at the overlapped region, which could be due to a commensurability adjustment of the layers in order to minimize the energy followed the thermal treatment. Alternatively, it is also possible that water, used as the solvent to transfer MoS_2 onto WSe_2 , got trapped between MoS_2 and WSe_2 monolayers, and its evaporation resulted in the corrugation of the top transferred layer during the thermal treatment. The high spikes of the cross-sectional profile in inset of Figure 1c reveal the profile of the corrugated structures.

Raman Features. For the Raman spectra we have used the notation of the monolayer modes using the symbols A_{1g}' , E' , and the notation of the bilayer for the higher order out of plane modes such as the A_{1g}^2 , since these modes are not Raman active in the monolayer. Figure 2a–d shows the Raman spectra of the double layer van der Waals solid excited with a 473 nm laser in four energy regions, where the curves from the top to bottom are MoS_2 region (blue), $\text{MoS}_2/\text{WSe}_2$ heterojunction before annealing (green; $\mu\text{M/W}$), $\text{MoS}_2/\text{WSe}_2$ heterojunction after annealing (red; cM/W), and WSe_2 region (black), respectively. The characteristic peaks for WSe_2 at about 250 cm^{-1} (E' and A_{1g}' degenerated mode) and those for MoS_2 located at 387 cm^{-1} (E' mode; in-plane vibration) and 402 cm^{-1} (A_{1g}' mode; out-of-plane vibration) are observed in individual monolayers of WSe_2 and MoS_2 . In addition, the layer-number sensitive mode A_{1g}^2 for WSe_2 at around 309 cm^{-1} (out-of-plane mode) has been reported only observable when the WSe_2 is a bilayer or thicker.^{29,30} A similar feature A_{1g}^2 for bulk MoS_2 is located at around 463 cm^{-1} .^{31–36} Furthermore, there is another characteristic peak for bulk MoS_2 at around 284 cm^{-1} in odd number of layers

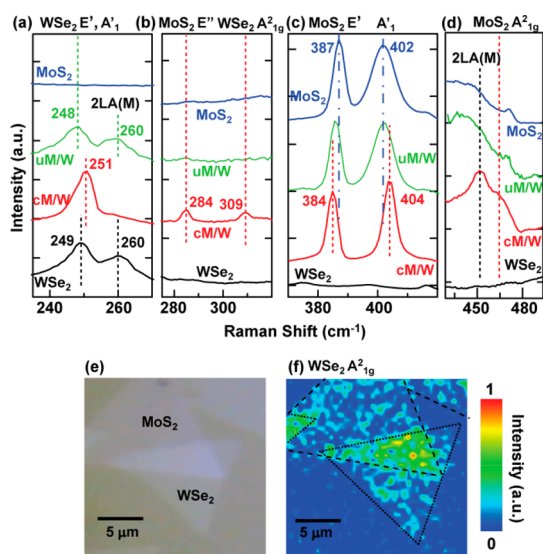


Figure 2. Raman spectra of the MoS₂/WSe₂ heterojunction. (a–d) Raman spectra for MoS₂ (blue), uncoupled MoS₂/WSe₂ heterojunction (green; μ M/W), coupled MoS₂/WSe₂ heterojunction (red; cM/W), and WSe₂ (black) from the top to the bottom plot. The curves are shifted for clarity. (e) Optical microscopic image for the MoS₂/WSe₂ heterojunction. (f) The spatial mapping of the Raman intensity for WSe₂ A_{21g} peak in the selected area shown in (e).

is called E'' and in even number of layers becomes E_g due to the symmetry involved.^{31–33} Our Raman results for either MoS₂ or WSe₂ region do not exhibit these characteristic peaks, confirming that WSe₂ and MoS₂ are monolayers. Note that the Raman band at 260 cm^{−1} observed at WSe₂ region (Figure 2a) and at about 450 cm^{−1} at MoS₂ region (Figure 2d) corresponds to the second order LA(M) phonon (2LA(M)).^{35–37}

It is observed that the Raman peaks for either MoS₂ or WSe₂ region show no obvious change after the thermal annealing at 300 °C as shown in Supporting Information Figure S2a, which implies that the annealing process does not cause significant structural defects or modification. For the heterojunction before annealing, we find that the Raman characteristic peaks are closely coinciding with the individual WSe₂ and MoS₂ regions, which implies that the layers are uncoupled (independent from each other). By contrast, after the thermal annealing process, the Raman spectrum for the heterojunction becomes significantly different from that for the individual WSe₂ and MoS₂ monolayers. First, the layer-sensitive characteristic peak A_{21g} for WSe₂ at 309 cm^{−1} clearly appear in Figure 2b. Second, the E' and A'₁ degenerated peak for the WSe₂ shows a blue-shift as shown in Figure 2a, and the A'₁ (E') for the MoS₂ shows blue (red)-shifts as shown in Figure 2c, respectively. Third, the anomaly E'' feature for MoS₂ is also observed in Figure 2b, and the layer-sensitive peak A_{21g} for MoS₂ is enhanced as found in Figure 2d.

The presence of the layer-sensitive Raman bands after thermal annealing strongly evidence that the

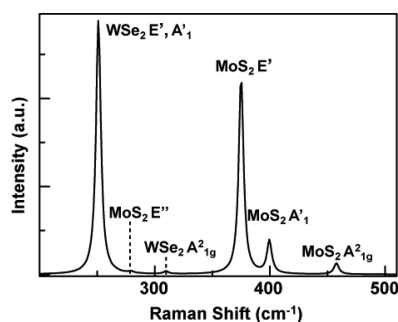


Figure 3. Raman scattering modes simulation of the MoS₂/WSe₂ heterojunction.

MoS₂ and WSe₂ interact with each other. It is also possible that some contaminants such as adsorbates trapped between MoS₂ and WSe₂ weaken the coupling between these two layers. After the thermal treatment, these contaminants are efficiently removed (as indicated by AFM), thus resulting in the commensurate stacking and the shifts in the Raman peaks. Figure 2e is the OM for the selected area for Raman mapping studies. Figure 2f shows the spatial mappings for the peak intensity of the Raman bilayer signature at 309 cm^{−1} for WSe₂ A_{21g} mode, and the Raman features is only observed and distributed uniformly in the stacked region, indicating that the peak is originated from the interlayer coupling in the new MoS₂/WSe₂ bilayer. It is noteworthy that the peak A_{21g} is Raman inactive in monolayer but become active in homobilayer or thicker layers. Here, the heterojunction stacking likely introduces a similar effect as in stacked homolayers, leading to the symmetry change and activation of the Raman features.

To further investigate the main features observed in the experimental Raman spectra of the MoS₂/WSe₂ junction, density functional theory (DFT) and density functional perturbation theory (DFPT) calculations were carried out using the plane wave code CASTEP as implemented in the Materials Studio package.³⁸ A hexagonal unit cell with one layer of MoS₂ and another of WSe₂ arranged in an AB stacking was considered under the local density approximation (LDA). To provide a reasonable description of the van der Waals interaction, we have considered a dispersion correction for LDA (LDA-D).³⁹ After the relaxation, due to the lattice mismatch between the monolayers, the MoS₂ lattice parameter suffered an expansion from 3.16 to 3.21 Å and the WSe₂ lattice contracted from 3.28 to 3.21 Å. The phonon dispersion and Raman scattering modes were calculated using the linear response approach for insulators.⁴⁰ The result of Raman scattering modes is shown in Figure 3, where all the modes, not the resonant second order or combinations of first order modes, are shown in the Figure 3. The characteristic peaks E' and A'₁ for WSe₂ and MoS₂ are exactly reproduced. The MoS₂/WSe₂ bilayer vibrations at 309 cm^{−1} (WSe₂ A_{21g}) is also clearly seen from

the simulation. Although the calculated frequencies are not exactly the same as obtained in experiments, the simulation results provide a good approximation of the Raman signals observed. The coincidence between the experimental and simulated results implies that the coupling exists in the MoS₂/WSe₂ bilayer heterojunction.

The Raman simulation in Figure 3 also presents the MoS₂ bulk vibration mode A²_{1g} at 458 cm⁻¹ and the anomaly E'' mode at 279 cm⁻¹. Comparing to our experimental results, although there have other Raman active modes near 460 cm⁻¹, the MoS₂ A²_{1g} mode still can be identified in Figure 2d for cW/M sample. The observed E'' mode at 284 cm⁻¹ in Figure 2b for cW/M sample can also be correlated to the simulation result. This peak is not normally observed because of the Raman geometry used (backscattering geometry) and also because it has low intensity. The observation on the E'' mode may indicate that the presence of the interlayer coupling could enhance its intensity. The observation on these Raman peaks for bulk MoS₂ is also an evidence of the existence of the interlayer coupling between MoS₂ and WSe₂.

It is known that the Raman E' peak of monolayer MoS₂ is sensitive to strain and strain could induce a red-shift in the E' modes that have been observed for MoS₂ monolayer or multilayers in other reports.^{33,41–43} The red-shift of the MoS₂ E' peak after the two layers are coupled (thermally treated) shown in Figure 2c indicates that a tensile strain has been imposed to the MoS₂. This also implies that the WSe₂ monolayer experiences a compressive strain and the E' peak of WSe₂ also shows an opposite blue-shift as shown in Figure 2a. As stated above, our simulation concludes the expansion of the MoS₂ and contraction of the WSe₂ (details in Methods) which explain in part the E' peak shift in MoS₂ and WSe₂ after the two layers are coupled.

Although the strain effect could explain the Raman shifts of the annealed hetero bilayer, we still cannot exclude the possibility of charge transfer between these stacked layers. The Raman A'₁ peak of MoS₂ blue-shifts and its intensity increases (relative to E'), thus indicating that MoS₂ is less n-doped (or a decrease in the electron concentration).^{44,45} The blue-shift of the WSe₂ Raman A'₁ peak implies that the WSe₂ may become less p-doped (Supporting Information Figure S3 shows that in our separate experiment, p-doping from AuCl₄⁻ causes a red-shift of Raman A'₁ peak in monolayer WSe₂). These phenomena suggest that the electrons transfer from MoS₂ to WSe₂, which is expected for the PN-junction composed by the p-type WSe₂ and n-type MoS₂.^{24–27} It is also noted that the effect of a compressive strain on E' and the n-doping effect on A'₁ in WSe₂ is not easily distinguishable since A'₁ and E' frequencies in WSe₂ are degenerate and both effects are expected to cause the blue-shift. However, the fact that the Raman shift of MoS₂ E'

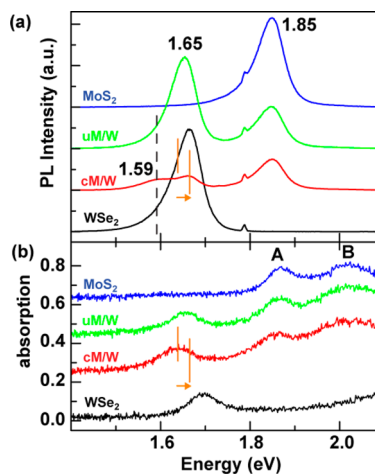


Figure 4. (a) Photoluminescence and (b) absorption spectroscopy of the MoS₂/WSe₂ heterojunction. The curves corresponding to MoS₂ (blue), noncoupled MoS₂/WSe₂ heterojunction (μ M/W) (green), coupled MoS₂/WSe₂ heterojunction (cM/W) (red), and WSe₂ (black) from up to down. The curves are shifted for clarity. The dashed line indicates the interlayer PL peak. The orange lines and arrow mark the anti-Stoke shift.

mode is larger than the A'₁ mode implies that the strain effect should play a major role than doping effect. On the other hand, the theoretical simulation including only the strain relaxation can well reproduce our experimental results, which further suggests that the strain effect is more significant. In any case, the shifts indicate the interaction between two stacked heterolayers. It is worth noting that our results show that the A'₁ and E' peak energies of MoS₂ do not seem to depend on the stacking angle between the two layers as shown in Supporting Information Figure S4, which is different from the recent studies on Raman spectra of bilayer MoS₂ which shows twisting angle dependence.^{46,47} This could be reasoned since the homobilayer might exhibit stronger interlayer coupling due to the same lattice constant for two layers (better matching between top and bottom layers).

Band Gaps and Band Alignments. To study the optical and energy band properties of the heterojunction, we performed the PL and absorption measurements. Figure 4a shows the PL spectra excited with a 532 nm laser and Figure 4b displays the absorption spectra for MoS₂, uncoupled MoS₂/WSe₂ heterojunction (μ M/W), coupled MoS₂/WSe₂ heterojunction (cM/W), and WSe₂ regions. The excitonic PL peaks for WSe₂ and MoS₂ monolayers at about 1.65 and 1.85 eV are clearly observed in the respective nonstacking region, and the peak energies also hold after annealing process as shown in Supporting Information Figure S2b. For the μ M/W region, the PL peak energy of WSe₂ or MoS₂ is very close to that for its corresponding layer, thus confirming that there is no strong layer coupling in the heterojunction. The slight suppression of the PL intensity for both MoS₂ and WSe₂ may be due to the

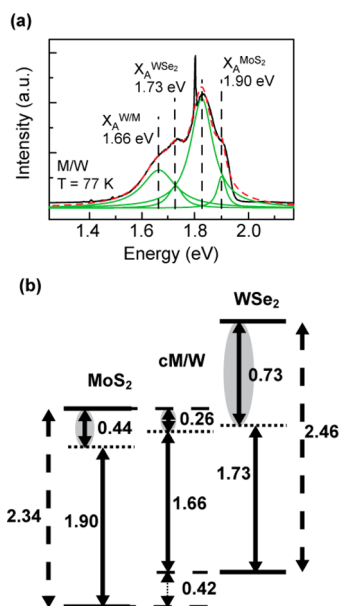


Figure 5. Schematic of the energy band alignment of MoS₂/WSe₂ heterojunction at 77 K. (a) The PL of cM/W sample (black) and the Lorentzian peaks fitting (red-dashed) at 77 K. The green lines are the composited peaks by using Lorentzian fitting. The black dashed lines indicate the emitted energy of MoS₂ and WSe₂ and cM/W. (b) The solid lines represent the conduction band and valence band of MoS₂ and WSe₂. The solid double arrow lines, dashed double arrow lines, and dot double arrow lines indicate the PL energy, band gap energy, and the valence band offset between MoS₂ and WSe₂ extracted from experimental results, respectively. The solid double arrow lines with gray background indicate the derived exciton binding energy.

defects/traps introduced by the stacking. For the cM/W sample, the PL intensity for both WSe₂ and MoS₂ is significantly lower compared to that of uM/W. In addition to the characteristic PL peaks from MoS₂ and WSe₂, an extra peak at a lower energy (~ 1.59 eV), and marked by a black dashed line is also observed. This PL peak appeared in previous work and it is attributed to the interlayer radiative recombination of the spatially separated carriers.²⁷ The excitons are excited separately in WSe₂ and MoS₂ by the incident laser. Since the MoS₂/WSe₂ junction is a type II heterojunction, the excited electrons in WSe₂ tend to accumulate in the conduction band of MoS₂ and the holes in MoS₂ in the valence band of WSe₂ at the interface as illustrated in Figure 5b. Therefore, the recombination of the electron–hole pairs at the interface gives lower energy than MoS₂ and WSe₂ itself. The interlayer PL peak reveals the nature of the coupling in the heterojunction.

The absorption spectrum for individual MoS₂ exhibits two absorptions peaks, A and B excitonic peaks at 1.87 and 2.01 eV, respectively. The WSe₂ has only one peak centered at 1.70 eV. As shown in Figure 4b, the absorption peak of the pristine WSe₂ is significantly higher (50–60 meV) than that of either μ W/M or cW/M, which might be due to that the WSe₂ is under MoS₂ and the dielectric environment is largely changed.

Moreover, a Stoke shift is found in cM/W sample between absorption peak (1.64 eV) and interlayer PL peak (1.59 eV), which further supports the radiative recombination between the WSe₂ and MoS₂. We should note that we found an anti-Stoke shift in the cM/W sample between the WSe₂ absorption peak (1.64 eV) and WSe₂ PL peak (1.66 eV), as marked with orange lines in Figure 4. The anti-Stoke shift implies that there might have some hot phonons in the optical level of WSe₂ under the heterojunction structure, which requires further experiments and theoretical work to clarify.

The observation on the interlayer PL peak not only show the strong evidence of the interlayer coupling, but also allow us to establish the energy band alignment of the MoS₂/WSe₂ heterojunction and the exciton binding energy of the junction as shown in Figure 5b. According to our previous work on STS²⁸ and μ -XPS,⁴⁸ we know that the energy band gaps for MoS₂ and WSe₂ are 2.34 and 2.46 eV, respectively, and the valence band offset is 0.42 eV. For consistency, we measure the PL spectrum at 77 K to set the energy band alignment. The PL spectrum at 77 K for each regime is shown in Figure 5a, and the extracted PL peaks are summarized in Figure 5b with solid double arrow lines. On the basis of these, we can determine the binding energy of the MoS₂/WSe₂ interlayer exciton, as marked by solid double arrow line with gray background, to clarify the discrepancy raised from previous works.^{49–52} We find that the MoS₂/WSe₂ interlayer exciton has a lower exciton binding energy 0.26 eV when compared to MoS₂ or WSe₂. The band alignment reveals the important role of the interlayer coupling, which is crucial for band engineering. In our work, we confirmed that the annealing process can enhance the interlayer coupling, which might result from reducing of layer distance or exclusion of interface residues in order to build van der Waals solids. Besides, we have also performed the experiments for the opposite stacking structure (WSe₂ on top of MoS₂) and this structure exhibits the similar behaviors in Raman (Supporting Information Figure S5) and PL (Supporting Information Figure S6), further corroborating the conclusions reached.

CONCLUSIONS

We fabricated the vertical MoS₂/WSe₂ heterojunction by stacking CVD-grown MoS₂ and WSe₂ triangular monolayers. The thermal treatment enhances the coupling between the two monolayers, based on the shifts observed in the Raman and PL spectra. Interestingly, the characteristic Raman signature at 309 cm^{−1} (WSe₂ A₂^{1g}), 463 cm^{−1} (MoS₂ A₂^{1g}), and 286 cm^{−1} (MoS₂ E'') suggest that the heterostructural stacking impose similar symmetry change as homostructural stacking. Together with the reported STS and μ -XPS results, the energy band alignment of the MoS₂/WSe₂ heterojunction and the

exciton binding energy were established. It is anticipated that the fundamental understanding of interlayer coupling and the band alignments in heterostructures

is crucially important for future applications and engineering of the devices based on two-dimensional materials and van der Waals solids.

METHODS

WSe₂/MoS₂ Monolayer Single Crystal Growth. WSe₂ and MoS₂ monolayer single crystal were separately growth by chemical vapor deposit method. The WO₃/MoO₃ powders (0.3/0.6 g) were placed in a quartz boat located in the heating zone center of the furnace. The Se/S powders were placed in a separate quartz boat at the upper stream side of the furnace and the temperature was maintained at 290/170 °C during the reaction. The sapphire substrates for growing were put at the downstream side, next to quartz boat. The gas flow was brought by an Ar/H₂/Ar flowing gas (Ar = 90 sccm, H₂ = 10 sccm/Ar = 70 sccm), and the chamber pressure was controlled at 7/40 Torr. The center heating zone was heated to 925/635 °C. After reaching growth temperature, the heating zone was kept for 15/30 min and the furnace was then naturally cooled down to room temperature.

Heterojunction Fabrication. MoS₂ on sapphire substrate was spin-coated with PMMA (950 K), and then heated on hot plate at 100 °C for 20 min. The sample was then tipped into NaOH (2 M) solution and kept at 100 °C for 1 h. After sapphire-etching by NaOH, MoS₂ with PMMA film was transferred into DI water twice, each step for 10 min, to dilute NaOH etching solution. And then MoS₂ with PMMA was transferred on sapphire with WSe₂ and heating at 100 °C on hot plate for 30 min to evaporate the water at the interface. Following, the sample was put into acetone at 60 °C for 30 min to remove the PMMA. Finally, the sample was rinsed with IPA and water, and dried with N₂ gas. Before annealing, the samples were examined by AFM, Raman spectroscopy, PL, and absorption spectroscopy. The as-prepared MoS₂/WSe₂ samples were then annealed in an hydrogen/Ar environment (atmosphere pressure; H₂:Ar = 1:4) at 300 °C for 4 h. The annealing temperature was selected at 300 °C to effectively remove the residuals but not too high to initiate the formation of alloys such as MoS_xSe_y or WS_xSe_y.⁵³

Characterizations. The AFM images were performed in a Veeco Dimension-Icon system. Raman spectra were collected in a confocal Raman system (NT-MDT). The wavelength of laser is 473 nm (2.63 eV), and the spot size of the laser beam is ~0.5 μm and the spectral resolution is 1 cm⁻¹ (obtained with a 1800 grooves/mm grating). The PL and differential reflectance spectra were measured in a homemade microscopy system. For room-temperature PL measurements, a 532 nm solid-state laser was focused to a spot size <1 μm on the sample by an objective lens (×100; N.A. = 0.9). The PL signals were then collected by the same objective lens, analyzed by a 0.75 m monochromator and detected by a liquid-nitrogen-cooled CCD camera. The apparatus for the differential reflectance measurements are basically the same, except that the light source was replaced by a fiber-coupled tungsten-halogen lamp. For low-temperature PL measurements, the sample was cooled down to *T* = 10.8 K in a low-vibration cryogen-free cryostat. The objective lens for low-temperature measurements is a long working distance objective lens with N.A. = 0.42.

Phonon Dispersion and Raman Scattering Modes Simulation. The density functional theory (DFT) and density functional perturbation theory (DFPT) calculations were carried using the plane wave code CASTEP³⁸ as implemented in the Materials Studio package. A hexagonal unit cell with one layer of MoS₂ and another of WSe₂ arranged in a AB stacking (similar to the one observed in bulk crystals of trigonal prismatic transition metal dichalcogenides) was considered under the local density approximation (LDA) using the Ceperly-Alder-Perdew and Zunger (CA-PZ) functional^{54,55} with 6X6X3 Monkhorst-Pack K-points and a plane waves cut off of 720 eV with a norm-conserving pseudopotential. The structure was relaxed, including the cell, until the forces became smaller than 0.01 eV/Å and with self-consistent energy tolerances less than 5 × 10⁻⁷ eV/atom. A vacuum of 16 Å between the cells was considered. The electronic

structure results obtained for the individual layers and bulk are in agreement with those reported by other groups within the LDA formalism.^{56,57} To provide a reasonable description of the van der Waals interaction, we have considered a dispersion correction for both LDA (LDA-D)³⁹ and for general gradient approximation (GGA-PW91)⁵⁸ finding that LDA provides a better description for the interlayer distance than LDA-D and corrected GGA-PW91, as described in a previous publications.^{35,59} The phonon dispersion and Raman scattering modes were calculated using the linear response approach for insulators.⁴⁰ After the relaxation, due to the lattice mismatch between the monolayers, the MoS₂ lattice parameter suffered an expansion from 3.16 to 3.21 Å and the WSe₂ lattice contracted from 3.28 to 3.21 Å. The expansion of the MoS₂ and contraction of the WSe₂ explain in part the shifts in some of the modes found in the Raman signal due to strain. Nevertheless, the results obtained here provide a good approximation of the Raman signal observed.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: AFM image for the stacked area of the as-transferred MoS₂/WSe₂ sample; Raman and PL spectra for the WSe₂ and MoS₂ areas before and after annealing process; schematics and AFM images of the WSe₂ triangular flake after the doping process of immersion in a AuCl₄⁻ solution; extracted peak positions of Raman A₁' mode (upper) and E' mode of MoS₂ with twist angle between MoS₂ and WSe₂; Raman and PL spectra of the WSe₂/MoS₂ heterojunction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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